XXVII. *On the Specific Heat and Heat of Transformation of the Iodide of Silver*, AgI, *and of the Alloys, or Compounds*, $Cu_2I_2.AgI$; $Cu_2I_2.2AgI$; $Cu_2I_2.3AgI$; $Cu_2I_2.4AgI$; $Cu_2I_2.12AgI$; $PbI_2.AgI$.

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In a series of papers printed in the Proceedings of the Royal Society for the years 1877, 1879, 1881, Mr. G. F. Rodwell has investigated the expansion and contraction by heat of the silver iodide, AgI; of certain chlorobromiodides of silver; and of certain alloys of silver iodide, with lead iodide, and copper iodide. Analogous researches were made by us on the substances $HgI_2.2AgI$; $HgI_2.3AgI$; $HgI_2.Cu_2I_2$;* which, when heated to a certain temperature, change their colour. $HgI_2.2AgI$ and $HgI_2.3AgI$, at about 50° C., change from canary-yellow to red, and $HgI_2.Cu_2I_2$, at about 70° C., changes from red to a chocolate colour. For temperatures below and beyond the colour-change the co-efficient of expansion and the specific heat are regular, but during a range of a certain number of degrees of heat in which colour-change and corresponding modification of structure take place, the substances undergo a very notable expansion and absorb a great quantity of heat.

It seemed to Mr. Rodwell, and to us, that it would be interesting to make a calorimetric study of those substances whose expansion and contraction he had determined, and Mr. Rodwell having kindly furnished us with the specimens which he employed in his researches, we have briefly described in this paper the method and results of our calorimetric determinations.

During the operation of heating, the substance was contained in a vertical double cylinder of brass, 3 centims. in diameter and about 12 centims. long (fig. 1, p. 1176). The substance to be examined, made into small rods, was arranged round the reservoir of a thermometer, whose stem passed through a cork which closed the upper end of the brass cylinder. At the lower end this cylinder was closed by two small double doors which could be opened by a spring, and thus allowed the substance to fall out. The

* M. Bellati and R. Romanese. Atti del R. Istit. Veneto (1880), ser. v., vol. vi.; Nuovo Cimento (1880), ser. iii., vol. viii.

brass cylinder was introduced into another very long brass cylinder, heated externally and at the lower end by water or paraffine, and closed by a cork. The stem of the thermometer, passing through this cork, supported at a convenient height the inner cylinder.

This manner of heating the substance is, indeed, somewhat slow; but we adopted it because it is very easy to maintain the temperature constant for a long time, and because it allowed us to carry the substance, protected by the cylinder, from the heating apparatus to the calorimeter, in which it was allowed to fall, without any appreciable loss of heat.

We used a GEISSLER'S thermometer graduated to $\frac{1}{2}^\circ$ C.; but the temperatures were referred to the air-thermometer after having accurately compared our GEISSLER'S thermometer with a JOLLY'S air-thermometer.

The calorimeter (fig. 2) was a copper cylinder containing about 125 grms. of water, furnished with a movable cover, and was contained in a tin cylinder surrounded by water. For stirring the water a horizontal frame of copper wire covered by a brass net was moved up and down by a handle. The substance fell upon this net, and was moved in the water with the stirrer.

The thermometer in the calorimeter was graduated to $\frac{1}{10}^\circ$ C., and was accurately compared with a standard thermometer. The thermal capacity of the calorimeter, stirrer, and thermometer was 2·660 grms. Calorimetric experiments and calculations were made according to REGNAULT'S method, improved by WÜLLNER.* In order to diminish corrections the temperature of the water in the calorimeter was initially cooled below the outer temperature.

We have not described the physical properties of the bodies we have studied, because Mr. RODWELL has done so in his papers. We have only given the temperature range of the contraction and expansion by heat of each substance, derived from Mr. RODWELL'S private communications, and afterwards the results of our calorimetrical experiments.

Iodide of silver, AgI.

From 0° to 142° C., slight contraction.
,, 142° ,, 156°·5 C., great contraction.
,, 156°·5 ,, 527° C., expansion.

The calorimetric results are given in the following table, in which Q denotes the number of calories given out by unit weight of the substance in cooling from T to t° C. The rate of change of the specific heat of water for temperature is no doubt small, but still uncertain, and therefore we did not introduce any correction for it; but we give in the table the initial water temperature τ, so that the eventual correction is always possible.

* A. WÜLLNER, Wiedemann, Ann. (1880), vol. x., p. 284.

AgI.

No.	t.	T.	Q.		Difference.	τ.
			Observed.	Calculated.		
	° C.	° C.				° C.
1	15·67	67·68	2·994	2·990	+0·004	14·1
2	14·72	75·28	3·489	3·497	−0·008	12·9
3	14·03	110·68	5·713	5·705	+0·008	11·6
4	14·97	138·66	7·430	7·434	−0·004	11·0
5	20·68	163·15	14·90	14·87	+0·03	13·0
6	19·13	162·7	14·90	14·93	−0·03	11·4
7	21·01	264·0	20·66	20·67	−0·01	11·4
8	22·11	259·5	20·38	20·35	+0·03	11·0
9	21·87	259·7	20·35	20·37	−0·02	11·6

From these data we have calculated the mean specific heat c of AgI between any two temperatures t and T below 142°, the specific heat c_1 after change of structure, and the latent heat of change λ, supposing that the change happens at 150° C.

$$c=0{\cdot}054389+0{\cdot}0000372\ (T+t)$$
$$c_1=0{\cdot}0577$$
$$\lambda=6{\cdot}25.$$

The table shows also the calculated values for Q.

$Cu_2I_2.12AgI$.

From 0° to 95° C., very slight expansion.
„ 95° „ 124° C., neither expansion nor contraction.
„ 124° „ 228° C., notable contraction.
„ 228° „ 502° C., rapid expansion.

Our calorimetric results are given in the following table :—

$Cu_2I_2.12AgI$.

No.	t.	T.	Q.		Difference.	τ.
			Observed.	Calculated.		
	° C.	° C.				° C.
10	15·13	88·51	4·321	4·316	+0·005	12·7
11	16·69	88·81	4·238	4·242	−0·004	14·3
12	23·67	233·2	20·53	20·58	−0·05	12·2
13	24·00	234·3	20·67	20·62	+0·05	12·5
14	26·27	338·4	26·56	26·52	+0·04	11·5
15	24·81	327·9	25·97	26·00	−0·03	10·4

$$c=0{\cdot}05882\ \text{(mean, from 16° to 89°)}$$
$$c_1=0{\cdot}0580$$
$$\lambda=8{\cdot}31\ \text{(at 160°)}.$$

$Cu_2I_2.4AgI.$

From 0° to 180° C., slight expansion.
„ 180° „ 199° C., neither expansion nor contraction.
„ 199° „ 282° C., contraction.
„ 282° „ 493° C., expansion.

The following table gives a summary of our experiments :—

$Cu_2I_2.4AgI.$

No.	t.	T.	Q.		Difference.	τ.
			Observed.	Calculated.		
	° C.	° C.				° C.
16	15·47	98·94	5·129	5·110	+0·019	13·8
17	15 61	102·29	5·298	5·319	−0·021	13·9
18	16·83	173·72	10·093	10·094	−0·001	13·6
19	15·91	168·25	9·764	9·761	+0·003	12·8
20	17·67	293·5	26·62	26·57	+0·05	9·0
21	20·07	295·5	26·52	26·57	−0·05	11·6
22	20·91	339·9	29·58	29·64	−0·06	11·4
23	21·61	337·6	29·49	29·44	+0·05	12·2

$c=0·056526+0·0000410\ (T+t)$
$c_1=0·0702$
$\lambda=7·95$ (at 230° C.).

$Cu_2I_2.3AgI.$

From 0° to 194° C., expansion.
„ 194° „ 214° C., neither expansion nor contraction.
„ 214° „ 280° C., contraction.
„ 280° „ 494° C., expansion.

Our results are as follows :—

$Cu_2I_2.3AgI.$

No.	t.	T.	Q.		Difference.	τ.
			Observed.	Calculated.		
	° C.	° C.				° C.
24	14·48	60·59	2·846	2·846	..	13·7
25	13·85	179·12	10·781	10·747	+0·034	10·4
26	11·88	179·63	10·867	10·901	−0·034	8·4
27	17·00	290·0	26·27	26·27	..	8·7
28	19·31	289·9	26·13	26·13	..	11·2
29	20·28	338·3	29·59	29·58	+0·01	10·9
30	19·30	343·2	29·99	30·00	−0·01	9·8

$c=0·059624+0·0000280\ (T+t)$
$c_1=0·0726$
$\lambda=7·74$ (at 240° C.).

$Cu_2I_2.2AgI$.

From 0° to 221° C., expansion.
„ 221° „ 233° C., neither expansion nor contraction.
„ 233° „ 298° C., contraction.
„ 298° „ 496° C., expansion.

We obtained :—

$Cu_2I_2.2AgI$.

No.	t.	T.	Q.		Difference.	τ.
			Observed.	Calculated.		
	° C.	° C.				° C.
31	11·70	63·86	3·299	3·300	−0·001	10·6
32	13·10	64·06	3·227	3·226	+0·001	12·0
33	13·36	209·4	13·23	13·26	−0·03	8·7
34	15·12	209·3	13·17	13·14	+0·03	10·5
35	20·85	305·7	27·99	28·01	−0·02	11·3
36	18·24	306·9	28·29	28·27	+0·02	8·5

$c=0{\cdot}061035+0{\cdot}0000295\ (T+t)$
$\lambda=7{\cdot}88$.

$Cu_2I_2.AgI$.

From 0° to 256° C., expansion.
„ 256° „ 284° C., neither expansion nor contraction.
„ 284° „ 309° C., contraction.
„ 309° „ 324° C., neither expansion nor contraction
„ 324° „ 514° C., expansion.

Our results are as follows :—

$Cu_2I_2.AgI$.

No.	t.	T.	Q.		Difference.	τ.
			Observed.	Calculated.		
	° C.	° C.				
37	11·66	63·59	3·378	3·378	..	10·4
38	15·05	231·1	15·05	15·02	+0·03	9·2
39	15·46	229·2	14·81	14·85	−0·04	9·7
40	20·19	333·0	31·29	31·28	+0·01	8·1
41	22·26	332·7	31·11	31·12	−0·01	10·3

$c=0{\cdot}063099+0{\cdot}0000260(T+t)$
$\lambda=8{\cdot}67$.

Some experiments were also made with Cu_2I_2, but this substance, when heated, emits iodine vapour, and is therefore slowly decomposed. Its surface was covered by some oxide. The mean specific heat between 13° C. and 65° C. would be found 0·0684,

and between 13° C. and 148° C. 0·0686. The increase for temperature is therefore very little.

$PbI_2.AgI$.

From 0° to 118° C., expansion.
„ 118° „ 124° C., neither expansion nor contraction.
„ 124° „ 139° C., contraction, more rapid between 130° C. and 133° C.
„ 139° „ 144° C., neither expansion nor contraction.
„ 144° „ fusion, expansion.

Our determinations gave the following results :—

$PbI_2.AgI$.

No.	t.	T.	Q.		Difference.	τ.
			Observed.	Calculated.		
	° C.	° C.				
42	12·65	65·82	2·566	2·558	+0·008	11·7
43	10·75	62·56	2·484	2·491	−0·007	9·9
44	11·93	113·0	4·909	4·904	+0·005	10·2
45	13·45	112·9	4·815	4·823	−0·008	11·8
46	13·75	171·1	10·531	10·529	+0·002	10·2
47	15·66	171·4	10·455	10·456	−0·001	12·2
48	15·09	242·4	14·52	14·51	+0·01	10·5
49	13·90	242·0	14·52	14·54	−0·02	9·3

$c=0{\cdot}047458+0{\cdot}00000839\ (T+t)$
$c_1=0{\cdot}0567$
$\lambda=2{\cdot}556$.

The following table recapitulates our results. θ_1 and θ_2 are the temperatures at which the structure-change commences and ends according to Mr. RODWELL'S experiments.

Composition of the substance.	Percentage of AgI.	θ_1.	θ_2.	c.	c_1.	λ.
		° C.	° C.			
AgI	100	142	156·5	$0{\cdot}054389+0{\cdot}0000372\ (T+t)$	0·0577	6·25
$Cu_2I_2.12AgI$	88·1	95	228	0·05882 (from 16° to 89°)	0·0580	8·31
$Cu_2I_2.4AgI$	71·2	180	282	$0{\cdot}056526+0{\cdot}0000410\ (T+t)$	0·0702	7·95
$Cu_2I_2.3AgI$	65·0	194	280	$0{\cdot}059624+0{\cdot}0000280\ (T+t)$	0·0726	7·74
$Cu_2I_2.2AgI$	55·3	221	298	$0{\cdot}061035+0{\cdot}0000295\ (T+t)$	..	7·88
$Cu_2I_2.AgI$	38·2	256	324	$0{\cdot}063099+0{\cdot}0000260\ (T+t)$	..	8·67
$PbI_2.AgI$	33·8	118	144	$0{\cdot}047458+0{\cdot}00000839\ (T+t)$	0·0567	2·556

From these data we may deduce the following conclusions.

I. The specific heat of the bodies we experimented on, below the point at which a change of structure commences, increases with the temperature.

II. This specific heat for the alloys of silver- and copper-iodide diminishes when the percentage of silver-iodide increases, but if we calculate the specific heat of the alloys from the specific heats and the proportion of components, we approach only roughly to the true values. It seems that the coefficient of $T+t$ generally increases with the percentage of AgI. The coefficient 0·000028, for $Cu_2I_2.3AgI$, appears to be less than that for $Cu_2I_2.2AGI$; but, perhaps, that is due to some uncertainty in the experiments, notably Nos. 25 and 26. The coefficient for $Cu_2I_2.12AgI$ was not determined, owing to the low temperature of change of this substance.

III. The value of the heat of change, λ, for $PbI_2.AgI$ is *less*, and for the alloys of silver- and copper-iodide is *greater* than for pure iodide of silver. This singular result leads to the assumption that some or all of the alloys of copper- and silver-iodide *are real chemical or molecular compounds.* Starting from the values of λ for AgI and for $Cu_2I_2.AgI$, and calculating the values of λ for the other alloys, considered as mixtures of AgI and $Cu_2I_2.AgI$, we find the numbers 7·99, 7·62, 7·38, 6·72 respectively for $Cu_2I_2.2AgI$, $Cu_2I_2.3AgI$, $Cu_2I_2.4AgI$, $Cu_2I_2.12AgI$. These numbers differ from those given above, but making allowance for errors of observation, for want of the values of c_1 respecting $Cu_2I_2.AgI$ and $Cu_2I_2.2AgI$, and for the uncertainty of the temperature for which λ is computed, it is perhaps probable that at least $Cu_2I_2.2AgI$ and $Cu_2I_2.3AgI$ might be considered as mixtures of AgI and $Cu_2I_2.AgI$. The uncertainty in the temperature of change is chiefly influential in $Cu_2I_2.4AgI$ and $Cu_2I_2.12AgI$, for which bodies the interval of temperature between the commencement and end of the change of structure exceeds 100° C. Moreover, for these substances c_1 is small, and the coefficient of $T+t$ in the value of c has not been determined for $Cu_2I_2.12AgI$, and is somewhat uncertain for $Cu_2I_2.4AgI$, owing to discrepancy in the experiments Nos. 16 and 17. For these reasons the values of λ deduced from observation for those two substances do not pretend to great accuracy.

IV. The values of c_1 increase with the percentage of Cu_2I_2; and in the case of AgI and those alloys of AgI and Cu_2I_2 for which c_1 was determined, the values of c_1 are smaller than the values of c computed for corresponding temperatures. The difference between c_1 and c, extended beyond the temperature of change, diminishes as the percentage of Cu_2I_2 increases. It is therefore probable that c_1 does not much differ from c in $Cu_2I_2.2AgI$ and $Cu_2I_2.AgI$, for which the values of λ are computed on this assumption.

V. For $PbI_2.AgI$ the value of c_1 is greater than the value of c for corresponding temperatures.

Perhaps other conclusions may be derived by comparing our calorimetric results with those of thermic expansion and contraction obtained by Mr. RODWELL; but

Mr. RODWELL'S last paper had not been published *in extenso*, when the present paper was written.

Before concluding, we beg to express our deepest gratitude to Mr. RODWELL, who kindly sent us the substances he had studied, and to Professor FR. ROSSETTI, Director of the Physical Institute of Padua, who afforded us every facility for the execution of our experiments.

Fig. 1.

Fig. 2.